IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT : Phillip Mackie *et al*

SERIAL NO. : 10/009,399   EXAMINER : D.S. Nakarani

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TITLE : TREATED CLOSURES 2

DECLARATION UNDER 37 C.F.R. 1.132

COMMISSIONER FOR PATENTS
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I, Rosalind Ma as evidenced by my signature below, declare the following:

1.   I received a Bachelor of Science in Chemistry (Hons) from the University of Western Australia in 1997. I received a Ph. D. degree in Applied Science from the University of South Australia in 2002.

2.   Since 2004 I have worked as Technical Services Manager at Vinpac International Pty Ltd in Angaston, SA, Australia where I am responsible for:

- The running of a NATA certified laboratory with a staff of 14 people
- Managing all customer complaints relating to cork
- Troubleshooting technical issues relating to cork and the analytical lab
- Management of R&D projects

3.   From 2002- 2004 I worked as a R&D Coordinator at Vinpac International Pty Ltd in Angaston SA, Australia where I was responsible for   .

- The coordination and management of R&D projects
- Identifying new capabilities and developing new methods to improve efficiency
- Identifying new R&D projects to further the company's market competitiveness
- Identifying any packaging issues and developing contemporary solutions and, where required, implementing corrective action and follow-up

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4.   From Feb 2000 – Dec 2000, I was an Assistant Research Scientist in the Ian Wark Research Institute at the University of South Australia, Mawson Lakes. My research focused on the development of a new coating for cork.

5.   I have reviewed the above-noted application serial number 10/009,399 and the subject matter corresponding to the currently pending claims in the application.

6.   Attached as Exhibit A to this Declaration is a copy of my curriculum vitae.

7.   I have reviewed the reference that is the mentioned in the rejection of the claims in the subject patent application, namely, Feder, US Pat. No. 5,140,061.

8.   In order to determine whether the absorption of trichloro anisoles (TCA) is of a chemical nature, various functional groups were investigated for their ability to attract TCA. Glass wool was treated with an organosilane that contained a certain functional group. Organosilanes are practical materials to surface modification, and have been well studied in the modification of glass surfaces (Plueddemann, E. P., 1991, *Silane Coupling Agents,* 235). Organosilanes contain hydrolysable groups (X) and nonhydrolysable organic groups (R). The hydrolysable groups are normally methoxy or ethoxy. These groups hydrolyse to form a hydroxy functionality which bonds with polar surfaces such as glass. This leaves the organic group exposed on the surface.

$$R_nSiX_{(4-n)}$$
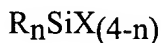
where R = organic group
X = hydrolysable group

9.   The reactions between the inorganic substance and the organosilane are described in the following scheme. The silanes are hydrolysed by dissolving them in a mixture of water and alcohol. A reactive silanol group is formed which can condense with other silanol groups to form oligomers (Plueddemann, E. P., 1991, *Silane Coupling*

Agents, 235). The residual hydroxy groups in the oligomers can then hydrogen-bond with OH groups of the substrate. A covalent linkage with the substrate is formed after drying.
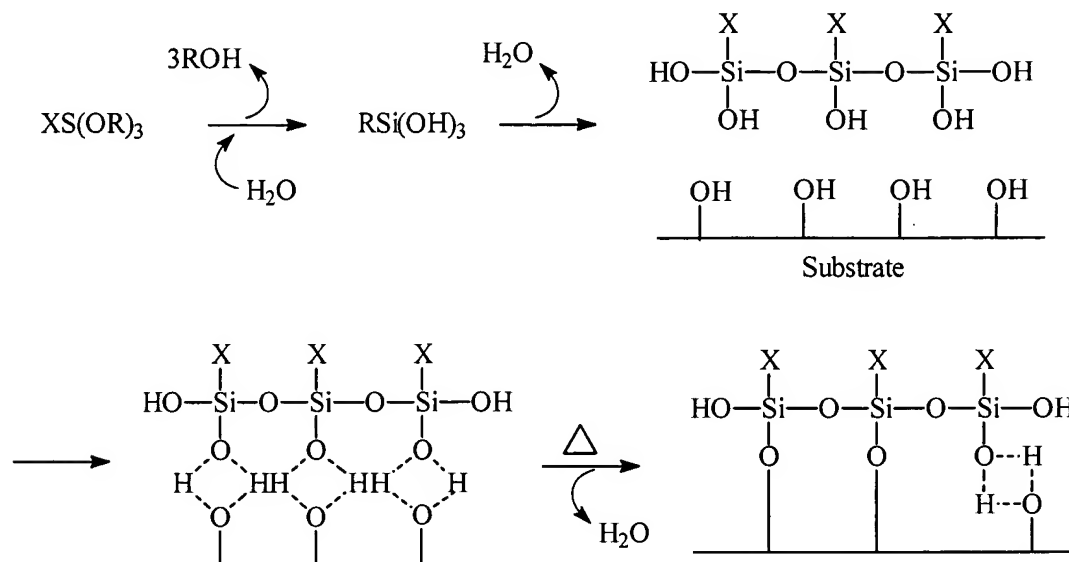

Scheme 1. Deposition of organosilanes onto a glass surface.

Once attached to the glass wool, the remaining exposed organic groups are free to react. In some cases it is possible for some of the functional groups to orientate towards the surface of the glass. A variety of different organic groups were attached to the glass wool.

10.   The glasswool was prewashed to remove any impurities then treated with functionalised silanes (Table 1). After the treatment, the glasswool was analysed by DRIFT to ensure that the silane had absorbed on the glass surface. No NH_3^+ vibration mode at $2150 cm^{-1}$ was observed in the any of the aminosiloxanes which indicates that the NH_2 group did not protonate and fold inwards to form a bond with the silica surface to give a cyclic structure (Chiang, et al., 1980, *J. Colloid and Interface Science*, 74(2):396 – 404).

Table 1 FTIR Results of the Silane Treated glasswool.

Silane	Wavenumber*	Assignment
Glasswool	2900cm^{-1} (vw)	C-H
	1400cm^{-1} (m)	Si-O-Si
	1300cm^{-1} (s)	Si-O-Si
	1000cm^{-1} (m)	Si-O-Si
A151 $CH_2\!\!=\!\!CH\!-\!Si\!-\!(OCH_2CH_3)_3$	3100cm^{-1} (w)	C-H (vinyl)
	1400cm^{-1} (m)	Si-O-Si
	1300cm^{-1} (s)	Si-O-Si
	1000cm^{-1} (m)	Si-O-Si
A174 (methacryloxypropyltrimethoxysilane structure)	2900cm^{-1} (w)	C-H
	1700cm^{-1} and 1625cm^{-1} (m)	C=O
	1400cm^{-1} (m)	Si-O-Si
	1300cm^{-1} (s)	Si-O-Si
	1000cm^{-1} (m)	Si-O-Si
A189 $HS\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	$2800 - 3000 \text{cm}^{-1}$ (w)	C-H
	2590cm^{-1} (w)	S-H
	1400cm^{-1} (m)	Si-O-Si
	1300cm^{-1} (s)	Si-O-Si
	1200cm^{-1} (m)	S-H
	1000cm^{-1} (m)	Si-O-Si
A1100 $NH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_2CH_3)_3$	$2200 - 3400 \text{cm}^{-1}$ (b)	NH_2
	$2850 - 2900 \text{cm}^{-1}$ (w)	C-H
	2600cm^{-1} (m)	NH_2
	1400cm^{-1} (m)	Si-O-Si
	1300cm^{-1} (s)	Si-O-Si
	1250cm^{-1}	NH_2
	1000cm^{-1} (m)	Si-O-Si
A1120 $H_2N\!-\!CH_2\!-\!CH_2\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	$2500 - 3400 \text{cm}^{-1}$ (b)	NH_2 and NH
	$2750 - 2900 \text{cm}^{-1}$ (w)	C-H
	2690cm^{-1} (w)	NH (secondary)
	2600cm^{-1} (w)	NH_2 (primary)

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	1400cm^{-1}(m)	Si-O-Si
	1300cm^{-1}(s)	Si-O-Si
	1000cm^{-1}(m)	Si-O-Si
A1170 (CH$_3$O)$_3$—Si—CH$_2$—CH$_2$—CH$_2$—NH—CH$_2$—CH$_2$—CH$_2$—Si—(OCH$_3$)$_3$	2500 – 3400cm^{-1}(b)	NH
	2750 – 2900cm^{-1}(w)	C-H
	2690cm^{-1}(w)	NH (secondary)
	1450cm^{-1}(m)	C-O
	1400cm^{-1}(m)	Si-O-Si
	1300cm^{-1}(s)	Si-O-Si
	1000cm^{-1}(m)	Si-O-Si
Z6040 CH$_2$—CH$_2$—CH$_2$—O—CH$_2$—CH$_2$—CH$_2$—Si—(OCH$_3$)$_3$	2750 – 2900cm^{-1}(w)	C-H
	1400cm^{-1}(m)	Si-O-Si
	1300cm^{-1}(s)	Si-O-Si
	1000cm^{-1}(m)	Si-O-Si

(vw) = very weak, (m) = medium, (s) = sharp, (b) = broad

11.   1 ml of a 1 mg/L and a 2 mg/L TCA/methanol solution was eluted through the silane treated glass wool followed by 1ml of methanol. 2ml of the eluant was collected in a sample vial and analysed by HPLC. The TCA peak appeared at 2.6 min at a wavelength of 230nm (Figures 1 and 2). A standard stock solution of 1 mg/L was prepared, and the HPLC instrument performed auto-dilutions. The experimental standard concentrations were 0.07 mg/L, 0.13 mg/L, 0.25 mg/L, 0.50 mg/L, 0.75 mg/L and 1.0 mg/L. The calibration curve was linear with a correlation coefficient of 0.99 (Figure 3).
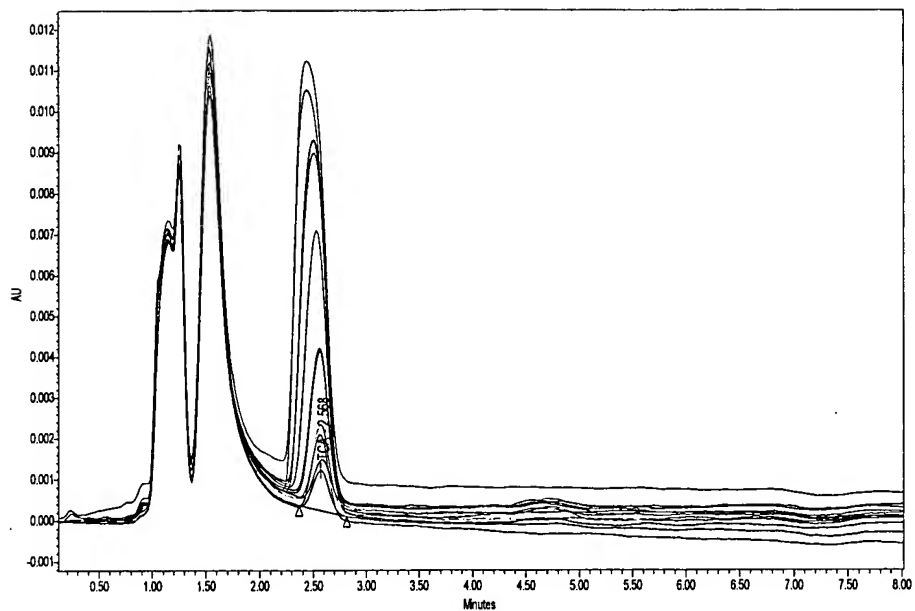
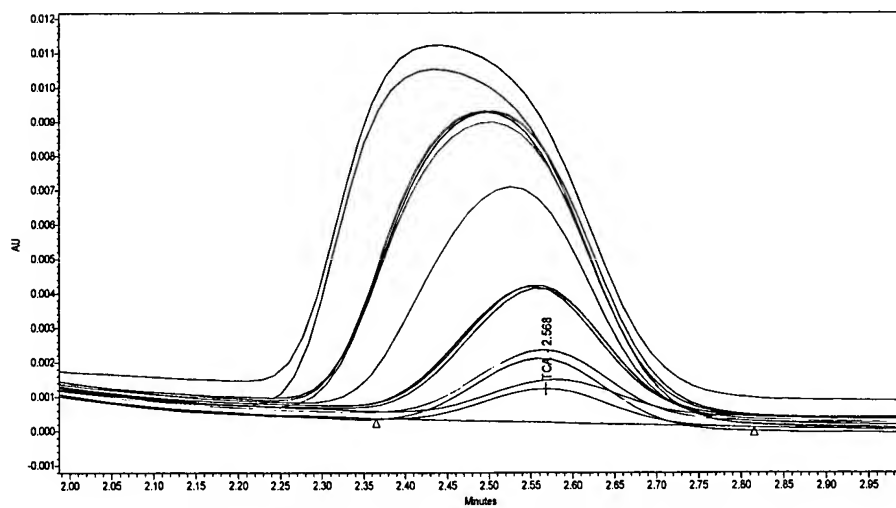**Figure 1. Chromatogram of TCA at different concentrations. (retention time = 2.6minutes)**

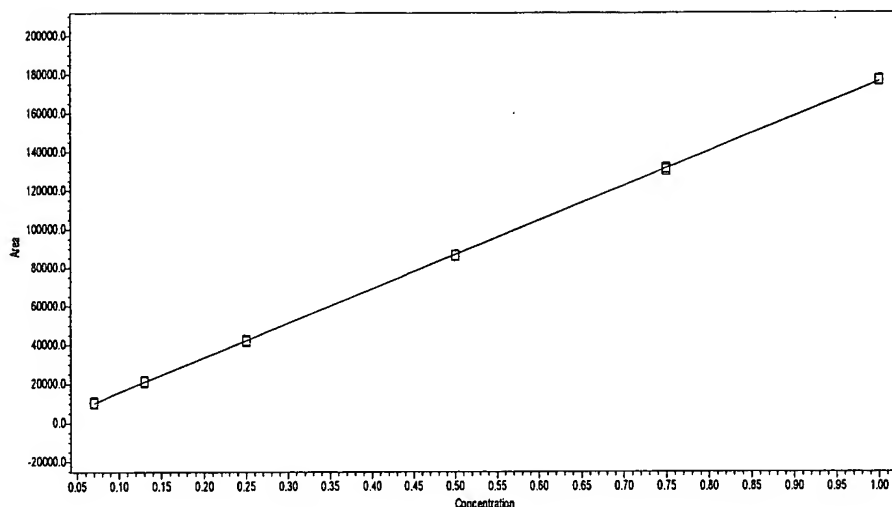**Figure 2. Enlargement of the TCA peak**

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Figure 3 Calibration curve of TCA concentration (mg/L) vs area of the TCA peak

12. All of the functional groups tested were able to hold a certain amount of TCA (Table 2). With the exception of the epoxy (Z6040) and the mercapto (A189) functional groups, which retained 35% and 42% respectively, all other groups were able to retain at least 1mg of TCA. However, when 2mg of TCA was eluted, all the functional groups became saturated with TCA. In general, the amino groups performed well, with aminopropylsilane (A1100) doing the best (96% retention of 2mg of TCA). Both primary and secondary amines were able to interact with the TCA; however, A1170, which contained one of each, did not have a higher absorbed level of TCA. It was possible that some of the amino groups crosslinked with each other preventing it from interacting with the TCA (Chiang, et al., 1980, *J. Colloid and Interface Science*, 74(2):396 – 404). The methacrylates also performed well, with absorbed TCA levels similar to the amines. The epoxy group failed to perform as well as the methacylate, which indicates that the oxygen atom must be a carbonyl oxygen. A column packed with untreated glass wool was eluted with the same TCA solutions as a control. The TCA recovery was 98%, indicating that the glass wool does not interact with TCA.

13. The most efficient mode of interaction between the TCA and the silane appears likely to be hydrogen bonding. In recent years, systematic investigations have shown that hydrogen bonding can exist in more that the conventional O—H···O or the N—H···O interactions (Plueddemann, 1991, *Silane Coupling Agents,* 235; Chiang et al.,

1980, *J. Colloid and Interface Science*, 74(2):396 – 404; Taylor, et al., 1982, *J Am Chem Soc*, 104(19):5063 – 5070; Desiraju, 1991, *Acc Chem Res*, 24:290 – 296; Steiner, **1997**, *Chem Commun*, 727–733. There is evidence that hydrogen bonding occurs via N—H⋯Cl, and under suitable conditions between C—H⋯O, C—H⋯N, and C—H⋯Cl. Taylor *et al.* surveyed published crystallographic data of 113 organic structures, which contain 661 cyrstallographically independent C—H atoms, and all structures contained at least one potential hydrogen acceptor atom (X = O, N, Cl, S). It was concluded that C—H⋯X contact is due to electrostatic attraction involving lone pair electrons preferably in a linear arrangement, but not necessarily. There was significant evidence to conclude that this type of contact exists with O, N and Cl. The evidence for S was found to be inconclusive. The geometrical characteristics, the spectroscopic and *ab initio* studies were found to be consistent with those of O—H⋯O hydrogen bonds and therefore it is reasonable to describe these C—H⋯X contacts also as hydrogen bonding (Taylor, *et al.,* 1982, *J Am Chem Soc*, 104(19):5063 – 5070). The factors that influence the occurrence of these C—H⋯X hydrogen bonding were identified. C—H groups adjacent to electron withdrawing atoms such as N were likely to form hydrogen bonding due to the decreased electron density around the C—H group. This is a significant factor especially in relation to amino acids, nucleosides and nucleotides where this type of bonding has been found to also exist (Jeffrey *et al.,* 1982, *Int. J. Biol. Macromol*, 4, 173-185; Allen *et al.,* 1979, *Acta Crystallogr*, Sect B, B35 2331-2339). In the presence of other proton donors such as O—H and N—H groups, C—H⋯X hydrogen bonding is less likely to occur, probably due to the preference of available proton accepting groups to bind with the O—H and N—H groups first. Hydrogen bonding between the NH and the chlorine substituents of TCA would explain the excellent TCA retaining abilities of silanes A1100, A1170 and A1120. The electron withdrawing affect of the carbonyl oxygen of silane A174 could result in hydrogen bonding between the (O=C)—H and the chlorine atoms on the TCA.

14.   A recent study in the absorption of chloroanisoles from wine by cork and other materials found that polyethylene film absorbed more TCA from TCA spiked wine that paraffin wax (Capone *et al.,* 1999, *Aust J Grape Wine Res*, 5, 91-98). Furthermore, it

was found that effectiveness of the absorption was directly related to the number of chlorines in the molecule. Therefore, pentachloroanisole was most efficiently absorbed and the least efficient was dichloroanisole. These results confirm that the interaction between the plastic and the TCA involves the chlorine atoms. It is possible that hydrogen bonding is occurring between the chlorine and the C—H hydrogen. This could also be the reason why the vinyl silane (A151) was also effective in retaining TCA.

Table 2 Summary of results from reactivity test

Silane	Conc. Of (TCA) (mg/L)	Detected Residual TCA (mg)	Absorbed TCA (mg)
A151	1	n. d.	1.00 (100%)
$CH_2\!=\!CH\!-\!Si\!-\!(OCH_2CH_3)_3$	2	0.32	1.68 (84%)
A174	1	n. d.	1.00 (100%)
H_2C, O ... $CH\!-\!O\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$, H_3C	2	0.17	1.83 (91%)
A189	1	0.58	0.42 (42%)
$HS\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	2	1.28	0.72 (36%)
A1100	1	n. d.	1.00 (100%)
$NH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_2CH_3)_3$	2	0.07	1.93 (96%)
A1120	1	n. d.	1.00 (100%)
$H_2N\!-\!CH_2\!-\!CH_2\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	2	0.33	1.67 (83%)
A1170	1	n. d.	1.00 (100%)
$(CH_3O)_3\!-\!Si\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	2	0.08	1.92 (96%)
Z6040	1	0.65	0.35 (35%)
$CH_2\!-\!CH_2\!-\!CH_2\!-\!O\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!Si\!-\!(OCH_3)_3$	2	0.71	0.29 (14%)

15.   These data clearly demonstrate that the reactive polymers of the present invention, namely A151 vinyl, A174 methacryl, A189 thiol, A1100 primary amino, A1120 primary and secondary amino, A1170 secondary amino and Z6040 epoxy react with trichloro anisoles (TCA).

16.   All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application, or any patent issuing thereon.

Submitted by

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Rosalind Ma, Ph.D.

Dated: 24/11/04